

# LIGHT LEATHER FROM ENZYME-UNHAIRD HIDES 2911

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## ABSTRACT

Hides have been unhaired with proteolytic enzymes without alkaline treatment and processed into shoe upper and handbag leathers.

The sides destined for shoe upper leather were given a full chrome tannage followed by a relatively high extract retannage. No adjustment was made in the fatliquoring. The leather was superior to opposite sides of the same enzyme-unhaired hides tanned by the regular process.

Enzyme-unhaired hides processed into handbag leather from the pickle, using the regular chrome tannage, produced leather comparable to the regular production.



## INTRODUCTION

The use of enzymes for unhairing has been investigated widely in an attempt to reduce stream pollution. Processes have been developed which can successfully remove hair from hides and skins without any alkaline pretreatment (1, 2, 3, 4).

Liming produces specific and desirable changes in collagen and is a fundamental step in leather manufacture. It is universally agreed that the omission of liming causes chrome-tanned leather to be flat and firm. Underliming produces the same effect to a lesser, but still noticeable, extent. Presumably the fibers have not been separated adequately. If this is correct it would follow that the larger the quantity of tanning material the better the leather. As evidence in support of this, it is easier to produce satisfactory sole than upper leather from enzyme-unhaired hides (3).

A characteristic of enzyme-unhaired hides is a loose grain which leads to drawn grain in the finished leather. Attempts to prevent drawn grain by the use of sodium polysulfide or sodium hydroxide in the soak have had limited success. Treating the hides in a salt solution before adding the sulfuric acid for pickling seemed to have a beneficial effect (5).

This paper will report efforts to produce satisfactory shoe upper and handbag leather from hides unhaired by enzymes in the absence of any alkaline treatment.

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For upper leather it was found that a full chrome tannage followed by a relatively heavy extract retannage improved the quality of the finished leather, although it was not consistently satisfactory. A regular chrome tannage, without extract retanning, yielded good quality handbag leather.

Although adjustments can be made for a specific kind of leather, the problem still remains to produce a variety of leathers by sorting in the blue from one beamhouse process.

## MATERIALS AND METHODS

### Side Upper Leather

*Hides.*—Fleshed, demanured, brined hides, weighing 25–35 lbs., were obtained from the M. A. Delph Company† and stored at 34°–36°F. until used.

*Unhairing.*—The hides were sided, soaked overnight and washed. In the first experiments they were treated with M-ZYME† in a rocker vat of a special design to keep the temperature uniform. The unhairing solution contained:

M-ZYME	200 Keratinase units/ml.
NaCl	5.0 percent solution basis
Borax	0.7 percent solution basis

The sides were rocked for about five hours and then held without rocking for an additional 18–19 hours at 86°F. The pH at the start was about 8.8 and dropped to about 8.4. Most of the hair remained on the hides, and this facilitated removal of the fine hair when the hides were unhaired on a beam. In later tests larger quantities of hides were unhaired in a drum essentially by the method described by Stellmach (2). The soaked sides were warmed in warm water and then placed in a drum in a solution containing 2 lb. borax,  $\frac{3}{4}$  to 1 quart of M-ZYME, and 0.1 to 0.25 lb. of a bacteriostat (Dowicide G) per 100 lb. of soaked, fleshed hide and 200 lbs. of water at 90°F. The drum was run for  $\frac{1}{2}$  hour and then 2–3 minutes per hour for the next five to six hours. Because of the drop in temperature overnight when working on a small scale the sides were removed from the liquor and steam was run in the drum to bring the temperature to 92–95°F. The sides were returned to the solution and allowed to stand without agitation for 24 hours. The hides were washed in the drum. This completely removed the hair and no beaming was necessary.

*Pickling.*—The sides were drummed in a 12 percent salt solution for  $\frac{1}{2}$  hour, then allowed to stand for five hours. One and one-half percent sulfuric acid was added in three feeds at  $\frac{1}{2}$  hour intervals and the drum was run continuously until all the acid had been added. The sides were allowed to remain in the pickle liquor overnight to obtain an equilibrium pickle with a pH of 1.7–1.8. This procedure appeared to reduce drawn grain (5). They were then horsed up to drain and

†M-Zyme is the trade name of the unhairing enzyme of Merck & Co., Inc. Mention of brand or firm names does not constitute an endorsement by the Department of Agriculture over others of a similar nature not mentioned.

stored in a cold room until needed. If the sides were to be tanned immediately, the chrome was added to a portion of the pickle liquor.

*Chrome tannage.*—Ten percent of Tanolin R† was dissolved in hot water and added to the sides in a drum in a 200 percent float in three feeds at 1/2 hour intervals. The drum was run for an additional 2 to 2-1/2 hours. Neutralization with small portions of sodium bicarbonate was begun. The sides were then allowed to stand overnight. After standing overnight, neutralization with sodium bicarbonate was continued until the pH was raised to 3.5. The tanned sides were taken to a local tannery where they were wrung and split.

*Vegetable retannage.*—When the retanning was carried out in the laboratory, 15 percent of a blend consisting of 1/3 each of powdered wattle, chestnut, and sulfited quebracho was used. Some sides were sent to the tanneries in the pickle and were tanned according to the regular process. All sides were fatliquored, with the regular fatliquor, paste dried, and finished at the tannery.

*Crushed Grain Handbag Leather.*—In these tests enzyme-unhaired sides were compared with the opposite sides unhaired by the regular lime-sulfide process. The left sides were enzyme-unhaired, pickled in the laboratory, as described above, and then sent to the tannery, together with the right sides "in the hair."

#### EXPERIMENTS AND RESULTS

*Side Upper Leather.*—In the first test four sides were chrome-tanned and vegetable-retanned in the laboratory, then fatliquored and finished at tannery "A." The evaluation of the leather is given in Table I. This leather was mellow and had a full, round feel. There was slight to moderate draw, and the break left something to be desired, but the tannery rated this leather as acceptable.

Six sides were sent to tannery "A" in the pickle and were chrome-tanned. Three were retanned lightly with vegetable tannins and three were given a larger amount of vegetable tans. The evaluation, given in the second section of Table I, shows that this leather was flat and firm. In another experiment two hides were sided, enzyme-unhaired and pickled. Two sides were chrome-tanned and vegetable-retanned in the laboratory. Opposite sides were treated in a similar way at tannery "A." The sides tanned in the laboratory were considerably more mellow and full than those tanned by the regular tannery procedure (Table I).

To confirm this variation, 12 hides were treated as in the previous test; that is, half of the sides were tanned in the laboratory and the opposite sides in the tannery. These sides were fatliquored together as a lot by themselves in order to avoid any chance of differential pickup of oil in a production pack. The results were essentially the same as in previous tests. The laboratory tanned sides were consistently mellow. A comparable test at another tannery, tannery "B," gave similar results except that there was less difference between the mellowness of the leather tanned in the laboratory and in the tannery, and all the sides were rather flat and firm.

TABLE I  
EVALUATION OF SIDE UPPER LEATHER FROM ENZYME UNHAIRED HIDES  
LABORATORY TANNED AND RETANNED WITH VEGETABLE EXTRACT

Side No.	Appearance	Temper	Fullness	Draw	Break	Tanners' Comments
61	good	mellow	full and round	slight	good	Temper very good.
62	"	"	"	moderate	"	Break not as good as desirable.
63	"	"	"	slight	fair-good	Leather acceptable.
64	"	"	"	"	"	
65*	poor	tinny	flat	moderate	good	Those with light vegetable
66*	"	"	"	"	"	retannage slightly mellow
67*	"	boardy, firm	"	slight	very poor	than others. Both considerably
68*	"	firm	"	"	"	firmer than normal. Nothing
69*	"	boardy, tinny	"	"	poor	outstandingly good or bad
70*	"	"	"	"	"	about this lot.
77†	poor	mellow	full and round	much	good	#77 and 80 substantially
78†	"	firm	flat	"	"	softer than mates even though
79†	"	"	"	none	fairly good	#77 and 80 were not staked
80†	good	mellow	full and round	"	good	while #78 and 79 were staked
						in the crust. Break poor
						except on #79.

\*Tanned and retanned at tannery "A." 65, 66, 67 light vegetable; 68, 69, 70 heavy vegetable.

†Tannery "A" vs. laboratory tannage and retannage. #77 and 80, laboratory; 78 and 79, tannery "A."

Table II gives the chrome and oil analyses of some representative samples split into three layers and chrome analyses of some composite samples. There do not appear to be any significant differences between the leathers in chrome content or distribution. The fat content is usually higher in the laboratory-tanned samples.

TABLE II  
CHROME AND FAT CONTENT OF LABORATORY  
AND TANNERY TANNED SIDE LEATHER

Side No.	Tanned at:	Chrome			Fat		
		Grain %	Center %	Flesh %	Grain %	Center %	Flesh %
61	Laboratory	2.6	2.7	1.8	11.0	7.6	19.7
67	Tannery	3.5	2.8	2.5	7.0	9.3	14.3
62	Laboratory	2.7	2.8	1.9	13.0	7.5	20.2
68	Tannery	2.7	2.7	1.7	7.6	1.7	12.6
		Entire Thickness					
77	Laboratory	1.8					
78	Tannery	2.5					
80	Laboratory	2.1					
79	Tannery	2.5					
		Composite*			Composite*		
	Laboratory	2.3			6.5		
	Tannery	3.0			4.6		

\*Composite of three sides.

Although it appears that acceptably mellow, chrome retan upper leather can be produced from enzyme-unhaired hides, the condition of the grain is still a problem. Frequently grain draw begins to occur during pickling, and while it can be overcome to a certain extent by paste drying, the break is often rather poor when the leather is mellow. The firm leather frequently has a good break. To some extent this is an inherent characteristic of mellow and firm leather.

**Handbag Leather.**—Two sides were enzyme-unhaired, chrome-tanned, and vegetable-retanned in the laboratory as given under upper leather. They were finished at tannery "C" as crushed grain handbag leather. This leather was very soft and mellow compared with the side upper leather resulting from the same tanning procedure, but was too firm and filled for a crushed-grain handbag leather. In another test two sides were processed through the pickle; one was tanned as before at the laboratory, and the other was tanned at the tannery by their straight chrome tannage. After finishing, as crushed grain leather, both sides were mellow, but the one with vegetable retan was too firm. In the next test, the left sides of six 25–35 lb. hides were enzyme unhaired, pickled at the laboratory and sent to the tannery. Opposite sides were unhaired at the tannery

by a lime-sulfide process. All of the sides were processed together by the regular procedure. The crushed grain handbag leather from these two lots was very good and was practically indistinguishable from regular production. This test was repeated using 55–65 lb. hides with the same results.

Table III gives the chemical analysis of some of these leathers. The chrome content and the pH of the leather from the tannery-unhaired sides was higher than that of the laboratory-unhaired sides. In the case of the fat the reverse was true.

TABLE III  
CHEMICAL ANALYSIS OF HANDBAG LEATHER

	T <sub>s</sub> °C.	Fat %	Chrome %	pH		
				Grain	Center	Flesh
Lime unhaired*	87–95	9.4	4.3	5.1		
Enzyme unhaired*	86–92	10.4	3.3	4.0		
Lime unhaired		11.4	4.3	4.14†	3.83†	4.05†
Enzyme unhaired		15.6	3.0	3.86†	3.74†	3.80†

\*Composite sample from opposite sides of 6 light hides.

†Average values from grain, center and flesh samples from opposite sides of two heavy hides.

It is striking that, in this instance, enzyme-unhaired sides required no adjustments in subsequent processing to yield commercially satisfactory leather.

#### SUMMARY

Superior results were obtained from enzyme-unhaired hides processed into shoe upper leather by a full chrome tannage followed by a high extract retannage. The results might be still further improved by adjusting the fatliquor.

No change in the regular process was required to produce a mellow handbag leather from enzyme-unhaired hides.

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